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Masayuki Yamane and Yoshiyuki Asahara
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Glass properties

Introduction

Glass can be made with excellent homogeneity in a variety of forms and sizes, from small fibers to meter-sized pieces. Furthermore, glass can be doped with rare earth ions and microcrystallites and a wide range of properties can be chosen to meet the needs of various applications. These advantages over crystalline materials are based on the unique structural and thermodynamic features of glass materials. Before discussing the special properties of glass, the fundamentals of glass materials are given in this chapter.

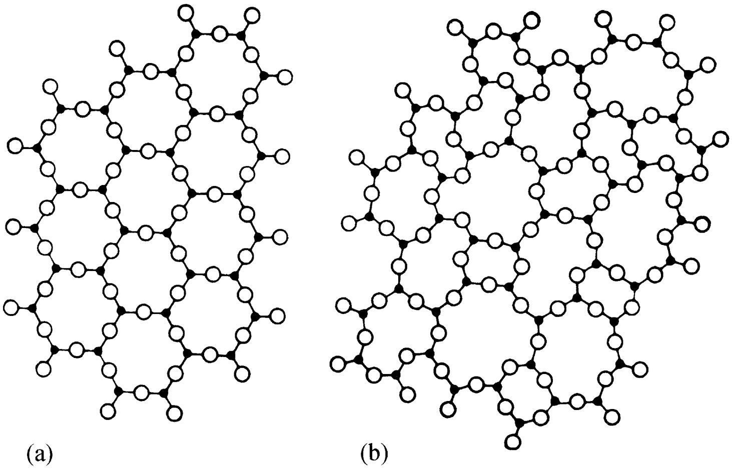
1.1 Features of glass as an industrial material

1.1.1 Structural features

1.1.1.1 Atomic arrangement

A glass is defined in ASTM [1] as ‘an inorganic product of fusion which has been cooled to a rigid condition without crystallization’. According to this definition, a glass is a noncrystalline material obtained by a melt-quenching process. Nowadays, noncrystalline materials that can not be distinguished from melt-quenched glasses of the same composition are obtainable by using various techniques such as chemical vapor deposition, sol-gel process, etc. Therefore, most glass scientists regard the term ‘glass’ as covering ‘all noncrystalline solids that show a glass transition’ regardless of their preparation method.

The words ‘noncrystalline solids’ and ‘glass transition’ suggest that a glass cannot be classified either in the category of crystalline materials such as quartz, sapphire, etc. or in the category of liquid. The atomic arrangement of a glass is different from those of crystalline materials and lacks long-range regularity, as schematically shown in Fig. 1.1 [2]. This is quite close to the



(a) (b)

Fig. 1.1. Schematic two-dimensional illustration of the atomic arrangement in (a) crystal and (b) glass [2].

atomic arrangement in a liquid. There is neither crystal lattice nor lattice point in the glass structure and therefore, instead of diffraction peaks a halo is seen in the X-ray diffraction patterns of a glass.

Substances which can form noncrystalline solids with the atomic arrangement shown in Fig. 1.1(b) and at an appreciable size are found in oxide, halide, and chalcogenide systems. The three-dimensional random network of strong bonds is developed by the constituent called the 'network former'. Some components called network modifiers can also participate in glass formation by acting to modify the glass properties. These components do not form networks but occupy thermodynamically stable sites as illustrated schematically in Fig. 1.2 or act as a replacement for a part of 'network former'.

Glass formation is possible, in principle, for a system of any composition provided that it contains sufficient of the component called 'network former'. Thus, a wide variety of multi-component glasses can be prepared to attain the desired properties by adjusting the chemical composition at a level below 1%. The lack of regularity of the atomic arrangement over a long range, i.e. the randomness of the structure, is essential to the understanding of the physical and chemical features relevant to those glasses which have the special properties that will be reviewed in this book.

The local environment of the modifying ions in Fig. 1.2 is different from site to site because of the lack in regularity of structure. Since an active ion doped in a glass occupies a similar position to the modifier ions, the absorption and emission spectra from the ion, if any, are broader than those from active ions

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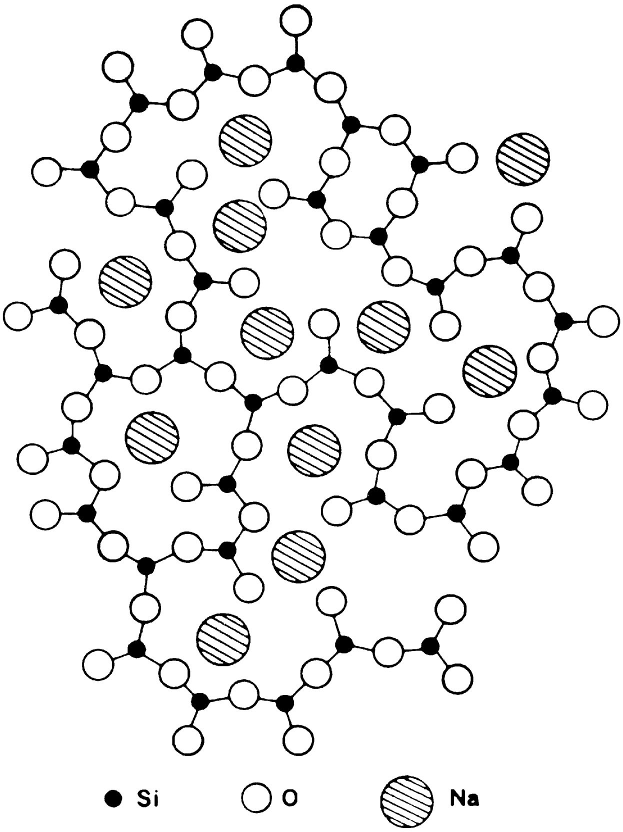

Fig. 1.2. Schematic two-dimensional illustration of the structure of a binary sodium silicate glass [3].

doped in a crystalline material as shown in Fig. 1.3 [4], a feature which is often advantageous in the preparation of a special glass.

The macroscopic properties of a glass such as optical transmission and absorption, refraction of light, thermal expansion, etc. are observed always equally in all directions, provided that the glass is free from stress and strain. That is, a glass is an isotropic material, whereas crystalline materials are generally anisotropic.

1.1.1.2 Chemical composition

Another important feature attributed to the uniqueness of the structure of glass is the flexibility of the chemical composition. Unlike crystalline materials, there is no requirement of stoichiometry among constituents provided that the electrical neutrality over the whole structure of a glass is maintained. Further-

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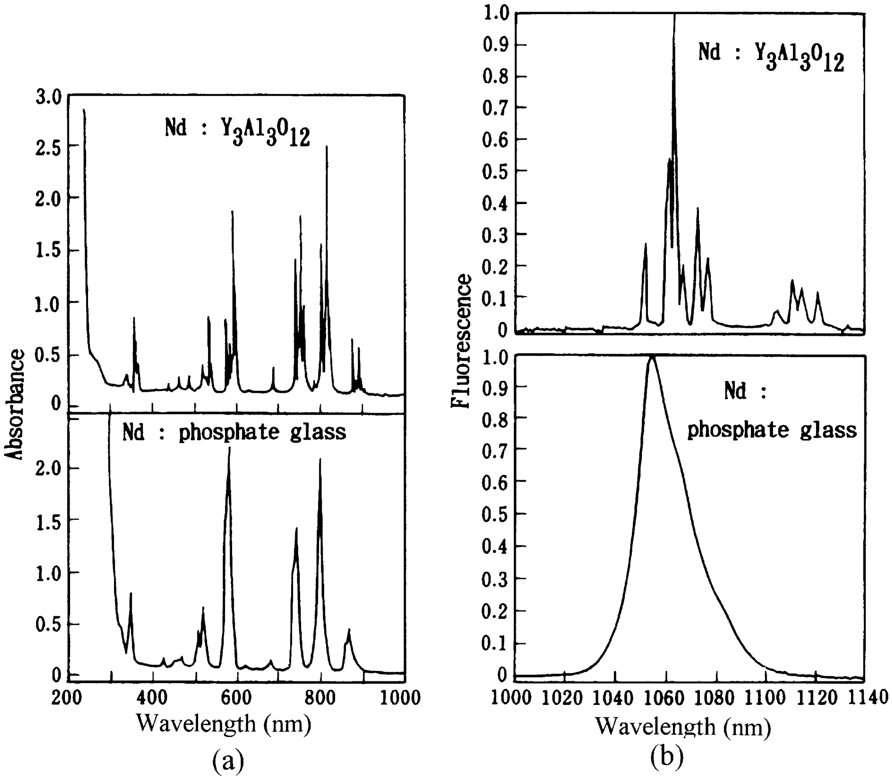

Fig. 1.3. Absorption and emission spectra of Nd ions in YAG crystal and phosphate glass. [Reprinted from M. J. Weber, *Handbook of the Physics and Chemistry of Rare Earth*, Vol. 4, ed. K. A. Gschneider, Jr. and L. Eyring (North-Holland Publishing Company, Amsterdam, 1979) p. 275.]

more, many properties of these multi-component glasses such as molar volume, thermal expansion coefficient, refractive index, etc. can be approximately described using the law of additivity of constituents [5]. These properties reflect the intrinsic nature of the respective constituents in proportion to their contents.

Property, P, of interest can be expressed approximately by Eq. (1.1) using the proportion of respective constituents, f_1, f_2, f_3, . . . , f_i, and factors representing their influence, p_1, p_2, p_3, . . . p_i, as;

$$P = \Sigma p_i f_i = p_1 f_1 + p_2 f_2 + p_3 f_3 + \ldots + p_i f i. \tag{1.1}$$

As there is no requirement on the stoichiometric ratio among constituents it is easy to dope active elements such as rare-earth or transition metal elements, semiconductor components, etc. Thus we can obtain a glass which has the unique properties inherent to the doped elements such as special color, emission of fluorescent light, high nonlinear susceptibility, etc.

The other feature that comes from the flexibility of glass composition is the ability to modify the properties of a glass through ion-exchange [6]. There are many stable sites for network modifier ions in a glass structure as shown in Fig. 1.2. For example, alkali ions that are easily thermally activated can move from one stable site to another within a glass. Such a movement of alkali ions within a glass structure enables us to replace alkali ions near the surface of a glass by other ions of the same valence, i.e. Na^+ by K^+; Na^+ by Ag^+; K^+ by $T1^+$, etc. This replacement of alkali ions in the original glass by other ions partially modifies the composition of the glass, and hence its properties. The technique, which will be described later in detail, is particularly important for the modification of optical and mechanical properties.

1.1.2 Thermodynamic features

1.1.2.1 Glass transition

A glass whose atomic arrangement lacks regularity over a long range generally has higher configuration entropy, and hence higher free energy, than a crystalline material of the same composition. In other words, a glass is a thermodynamicaly metastable material which remains un-transformed to its most stable state due to hindrance of the atomic rearrangement during the process of glass formation. The transformation of a glass to a crystal proceeds via nucleation and crystal growth under the driving force of the difference in free energy between crystal and glass, $\varDelta G_v$, which increases with the increase of super cooling $\varDelta T_r$. Both nucleation rate I_0 and crystal growth rate U are dependent on the viscosity η of a super-cooled liquid as well as on $\varDelta G_v$.

Since the viscosity η increases exponentially with decreasing temperature as shown in Fig. 1.4 [7], the influence of viscosity on the hindrance of atomic rearrangement increases with decreasing temperature, whereas the driving force for the transformation into crystal increases with decreasing temperature.

Thus the nucleation rate I_0 and crystal growth rate U are approximately expressed by the following Eq. (1.2) and (1.3) [8, 9]:

$$I_0 = k_1/\eta \exp(-g\alpha^3\beta/T_r(\varDelta T_r)^2) \tag{1.2}$$

where k_1 is a constant (typically about 10^{30} dyne cm), $T_r = T/T_m$, $\varDelta T_r = (T_m - T)/T_m$, g is a factor related to the shape of the nucleus and equal to $16\pi/3$ for a spherical nucleus, and α and β are dimensionless parameters given by

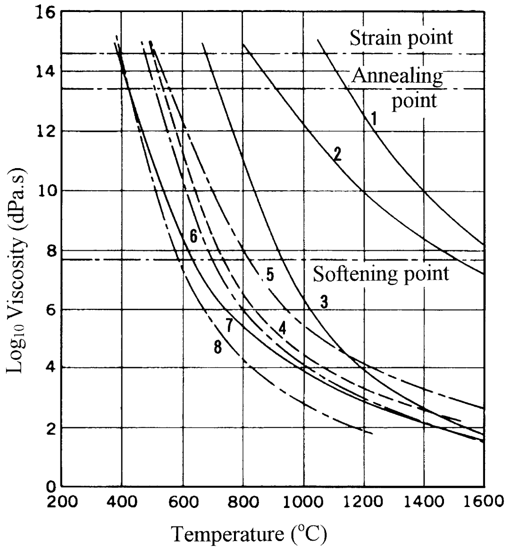

Fig. 1.4. Viscosity–temperature relationship of some commercial glasses. 1: Silicate glass; 2: High (96%) silica glass; 3: Aluminosilicate glass; 4: Soda-lime silicate glass (sheet glass); 5: Borosilicate glass; 6: Soda-lime silicate glass (electric bulb); 7: Lead-alkali silicate glass (electric use); 8: Lead-alkali silicate glass (high lead content). [7] [Reprinted from E. B. Shand, *Glass Engineering Handbook*, (McGraw-Hill Book Company, Inc., 1958) p. 16 copyright (1958) with permission from Corning Inc.]

$$\alpha = (N_A V_C{}^2)^{1/3}\sigma/\Delta H_{\mathrm{fM}} \tag{1.2a}$$

and

$$\begin{aligned}\beta &= \Delta H_{\mathrm{fM}}/RT_{\mathrm{m}}\\ &= \Delta S_{\mathrm{fM}}/R \end{aligned}\tag{1.2b}$$

where N_A is Avogadro's number, V_C is the molar volume of the crystal, σ is the crystal–liquid interface energy, ΔH_{fM} is the molar enthalpy of fusion and ΔS_{fM} is the molar entropy of fusion. For typical nonmetals, $\alpha\beta^{1/3}$ is about $0.5 \sim 0.7$.

$$U = f(RT/3N_A\pi\lambda^2\eta)(1 - \exp[\Delta H_{\mathrm{fM}}\Delta T/RTTm]) \tag{1.3}$$

where f is the fraction of the site at which the glass-to-crystal transition can take place on the crystal surface and $\Delta T = T_{\mathrm{m}} - T$, respectively.

In the temperature range near melting point T_{m}, the influence of $\Delta H_{\mathrm{fM}}/T_{\mathrm{m}}$ is predominant and, in the temperature range well below melting point, the influence of viscosity η is very large compared with the influence of $\Delta H_{\mathrm{fM}}/T_{\mathrm{m}}$. The schematic illustration of I_0 and U as a function of temperature gives curves which pass through maximum as shown in Fig. 1.5.

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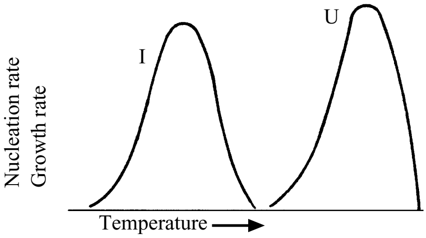

Fig. 1.5. Schematic illustration of temperature dependence of nucleation rate and crystal growth rate in a super-cooled liquid.

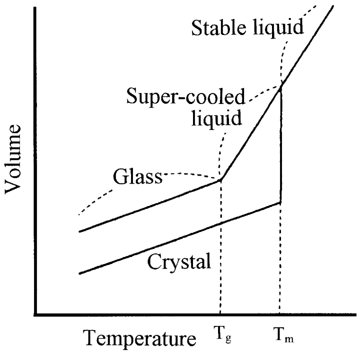

Fig. 1.6. Volume–temperature relationship of glass-forming liquid, and nonglass-forming liquid.

An important fact to be noted in the figure is that the temperature giving the maximum crystal growth rate (U) is higher than the one giving the maximum nucleation rate (I). When a viscous liquid is cooled from a high temperature, it passes through the temperature region of high crystal growth rate before nucleation takes place. When it passes through the temperature region of high nucleation rate, the crystal growth rate is already very low. Thus, a viscous liquid cooled at a sufficient rate further increases its viscosity to near or above 10^{14} dPa s without being transformed into a crystal. Once the viscosity reaches this value, even the alteration of the local atomic arrangement to equilibrate with temperature is not possible, resulting in the ‘frozen-in’ structure. Then the material behaves as a rigid and brittle solid, i.e. a glass. Physical and chemical phenomena occurring in a solid glass are no longer so sensitive to temperature change except for those that are enhanced by thermal activation such as the movement of alkali ions. Figure 1.6 shows the temperature dependence of the molar volume of a viscous super-cooled liquid, and uses glass as an example.

The transition from a viscous liquid to a solid glass is called the ‘glass transition' and the temperature corresponding to this transition is called the 'glass transition temperature', T_g. The reversible transformation from a glass to a viscous liquid also takes place if a glass is heated to a temperature above T_g.

Since the glass transition occurs as a result of the increase of viscosity and the rate of viscosity increase is dependent on cooling rate, the glass transition temperature, T_g, is not always the same even if the chemical composition is the same, but instead it is usually different, depending on the cooling rate of a liquid. A slow cooling allows enough time for a viscous liquid to alter its local atomic arrangement to attain the minimum free energy at the corresponding temperature, whereas a rapid cooling causes an increase of viscosity that is too quick for the local atomic arrangement to follow and results in a transition into a glass at a higher temperature.

The structure of a rapidly cooled glass is more open than that of a slowly cooled one because the 'freezing-in' of the atomic arrangement occurs at a higher temperature. The properties of a glass are therefore different from glass to glass, depending on the thermal history, even if the chemical composition is the same.

1.1.2.2 Thermal stability and structural relaxation

A glass obtained by cooling a liquid can transform into a crystal if re-heated to a temperature region that is well above T_g, where the nucleation and crystal growth takes place. Figure 1.7 shows an example of the crystallization of a glass detected by a differential thermal analysis (DTA) [10]. The exothermic peak observed in the temperature near 700 °C is attributed to crystallization. The sharpness of the peak and the difference between onset temperature and T_g reflect the thermal stability of a glass. If a glass is thermally unstable, the exothermic peak is sharp and the temperature difference is small.

On the other hand, if the temperature of re-heating is not high and remains near the glass transition temperature, which is well below the temperature giving high crystal growth rate, a glass remains uncrystallized but undergoes some change in atomic arrangement called structural relaxation [11]. The differences in structure and properties between glasses of different thermal history can be eliminated by the structural relaxation brought about by this heat treatment near the glass transition temperature. Figure 1.8 shows an example of such a change attributed to the structural relaxation [12]. It should be noted from this figure that the tuning of some properties of glass is possible by holding the glass at a temperature near the transition temperature.

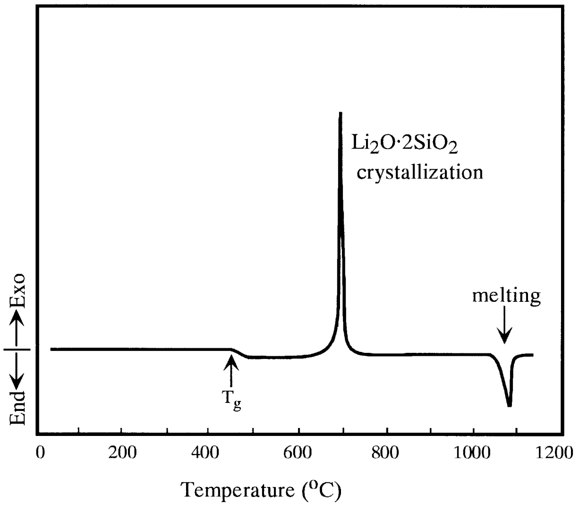

Fig. 1.7. Differential thermal analysis curve of $Li_2O–SiO_2$ glass heated at a rate of 10 °C min^{-1} [10].

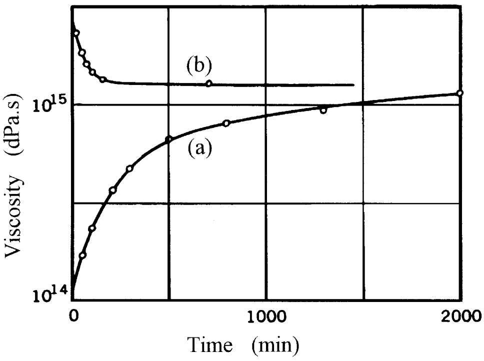

Fig. 1.8. Viscosity–time curves of a soda-lime silica glass at 486.7 °C [12]. (a) Newly drawn fiber; (b) Fiber stabilized at 477.8 °C for 64 h.

1.1.3 Optical features

1.1.3.1 Transparency

There is neither grain boundary nor interface within a glass structure and so the intrinsic scattering loss of a glass is very small. Therefore, a glass is, in principle, transparent to light in the wavelength region where the intrinsic absorption does not occur, i.e. between two intrinsic absorption edges determined by band-gap energy and the vibration energy of constituents.

Glasses of oxide and fluoride systems that have a wide gap between the conduction and valence bands are generally transparent to light in the visible and near infrared region, whereas those of the chalcogenide system have narrower band gaps and are generally translucent in the visible region but transparent in the near infrared and infrared regions as shown in Fig. 1.9 [13].

Owing to its high transparency to visible light, glass has long been used as the key material for various optical components. Taking advantage of the flexibility of composition, over two hundred kinds of commercial optical glasses have been developed to date.

The primary requisite for an optical glass are high purity and high homogeneity to allow the propagation of a light beam with minimum optical loss. The optical loss inherent to a glass of given composition consists of: (a) intrinsic absorption loss due to the transition of electrons from the valence band to the conduction band which is determined by the band gap energy between two bands; (b) absorption loss due to vibration of molecules; and (c) loss due to Rayleigh scattering. The values of these losses vary with the wavelength of light according to Eqs (1.4), (1.5) and (1.6), respectively [14–16];

$$\alpha(E)_{\mathrm{uv}} = \alpha_0 \exp[A_0(E - E_{\mathrm{g}})/kT] \tag{1.4}$$

where E is phonon energy, $\alpha(E)_{\mathrm{uv}}$ is the absorption coefficient at photon energy E, due to intrinsic absorption loss in UV region, E_{g} is band gap energy between the valence band and conduction band, k is Boltzmann constant, and α_0 and A_0 are constants [14].

$$\alpha(E)_{\mathrm{IR}} = \alpha_2 \exp(-E/E_2) \tag{1.5}$$

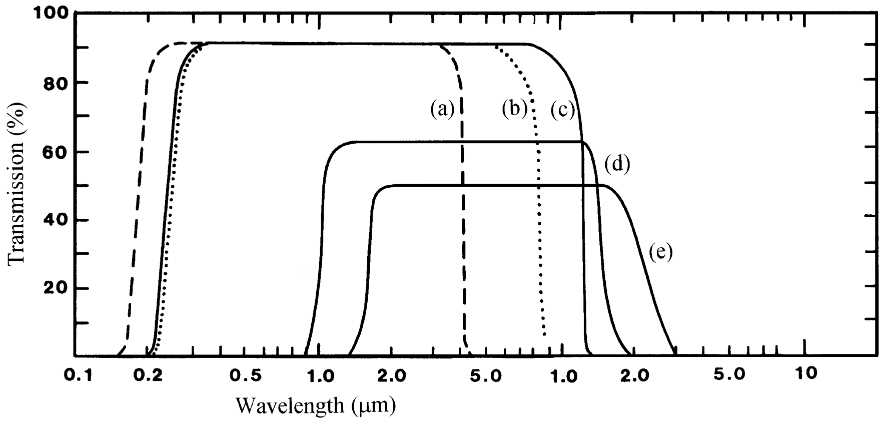

Fig. 1.9. Optical transmission curves of representative oxide, fluoride and chalcogenide glasses. (a) Silica glass, (b) $57HfF_4–36BaF_2–3LaF_3–4AlF_3$ (mol%) glass; (c) $19BaF_2–27ZnF_2–27LuF_3–27ThF_4$ (mol%) glass; (d) As_2Se_3 glass; (e) 10Ge–50As–40Te (atom%) glass. [Reprinted from M. G. Drexage, *Treatise on Materials Science and Technology*, Vol. 26, Glass IV (Academic Press, Inc., 1985) p. 151, copyright (1985) with permission from Academic Press, Inc.]